

CHAPTER 1

Introduction

1.1 Liquid crystals

Liquid crystals (LCs) are extensive in our day to day life with products ranging from mobile to flat panel display. Between the crystalline solid and isotropic liquid phases such materials display a distinctly different intermediate state [1-20]. These materials have some properties of crystalline solid like optical and magnetic anisotropy, periodical array of the molecules in a direction in addition to some characteristics of an isotropic liquid such as fluidity and viscosity. For this reason, the liquid crystalline phase is also known as ‘mesophase’ and the material that exhibit mesomorphic behavior is called ‘mesogen’. Due to the molecular shape anisotropy [4,17] and weak intermolecular interactions, the molecules self assemble in an organization with positional or orientational order which is much lower than crystalline ordering in a solid. The orientational ordering of molecules makes the material anisotropic while the low positional ordering permits the material to flow like a liquid. This dual combination of dynamic behavior and high degree of organization makes the liquid crystals very sensitive to various stimuli, such as temperature, electric and magnetic fields. Therefore, the self-assembling behavior, intermolecular interactions and sensitivity to external stimuli emerge these materials as potentially attractive for both fundamental findings of physics and widespread industrial applications [7,8,14,15,17].

In 1888, the Austrian botanist Friedrich Reinitzer [1], observed that an organic substance related to cholesterol melted to a cloudy liquid at 145.5°C and

became a transparent liquid at 178.5°C. Further the German physicist Otto Lehmann [2] realized that the cloudy liquid was a new phase of matter and coined the name “liquid crystal”. Over the last few decades several experimental and theoretical research on different mesophases and their properties grown enormously and still become a developing field in modern science.

Moreover, phase transitions also occur *via* spontaneous symmetry breaking process from one phase to another phase and an order parameter is a measure of the degree of ordering across the boundaries in a phase transition system. Therefore, for better understanding about the nature of phase transitions and related different phenomenon study of liquid crystal systems provide a fascinating area of research. In 1958 Alfred Saupe together with his advisor Wilhelm Maier [21-23] derived a basic molecular theory of liquid crystals without considering the presence of permanent dipoles. Later, McMillan [24] proposed a mean-field theory for smectics in 1971. De Gennes [25,26] expanded the Landau theory [27-28] of phase transitions into liquid crystals and got the Nobel prize in 1991 for his contribution to the understanding of liquid crystals and polymers. These molecular theories successfully describe molecular order in various liquid crystal phases, transitions among them, and elastic as well as hydrodynamic properties.

1.2 Classification of liquid crystals

Liquid crystals are broadly classified into two types, *viz.* ‘Lyotropic’ and ‘Thermotropic’. Lyotropic liquid crystals are biologically important and the transition between different phases can be obtained by changing the concentration of solvents. On the other hand in case of thermotropic liquid crystals the transformations are brought about by changing the temperature. The brief descriptions of each of these phases are given below.

1.2.1 Lyotropic liquid crystals

Lyotropic liquid crystals are among the promising representatives of multifunctional soft matter combining the capabilities of organized nano- and macroscale structures with unique magnetic, electrical and photophysical properties. They are solutions of amphiphilic molecules, where one end of the

individual molecule is hydrophilic and the other end is hydrophobic in an isotropic solvent [29-32]. The concentration of solution is one of the most important variable. The compound interacts with appropriate solvent at a certain concentration and the molecules arrange into spheres, rods or discs, called micelles. Generally, it is found in several biological objects *i.e.* chloroplasts, myelin sheaths of neurons and polypeptides. Lyotropic liquid crystals find applications in the studies of living matter of cell membranes and muscle reflexes as well as in biomedicine as transport drug delivery systems [33].

1.2.2 Thermotropic liquid crystals

Thermotropic liquid crystals are composed by organic molecules in a certain temperature range and the word “thermo” referred to phase transitions due to change in temperature. A general structural feature of such mesogens is a relatively rigid core, often incorporating aromatic groups and flexible terminal groups, often alkyl or alkoxy chains. In 1922 George Freidel [3] classified the thermotropic liquid crystals into three different categories *i.e.* nematic, cholesteric and smectic phase on the basis of molecular ordering.

1.2.2.1 Nematic phase

The nematic (N) phase is the simplest mesophase exhibiting least molecular ordering and highest symmetry among all the liquid crystalline phases. It is characterized by a long range orientational order with no long range positional ordering of the centre of mass of the molecules [34-36]. In this phase the constituent molecules tend to orient themselves along a preferred direction known as the nematic director \mathbf{n} . The director \mathbf{n} is the average local direction of long molecular axis representing the direction of the optic axis. The centre of mass of the molecules is arranged isotropically which indicates the absence of positional ordering. The nematic phase is also centro-symmetric as the system is indistinguishable with an inversion of the director *i.e.* $\mathbf{n} = -\mathbf{n}$. Figure 1.1 shows the schematic diagram of molecular order in nematic liquid crystals. Generally, nematic phase is optically uniaxial, but in biaxial nematic phase it is characterized by three orthogonal directors – a primary \mathbf{n} and two secondary.

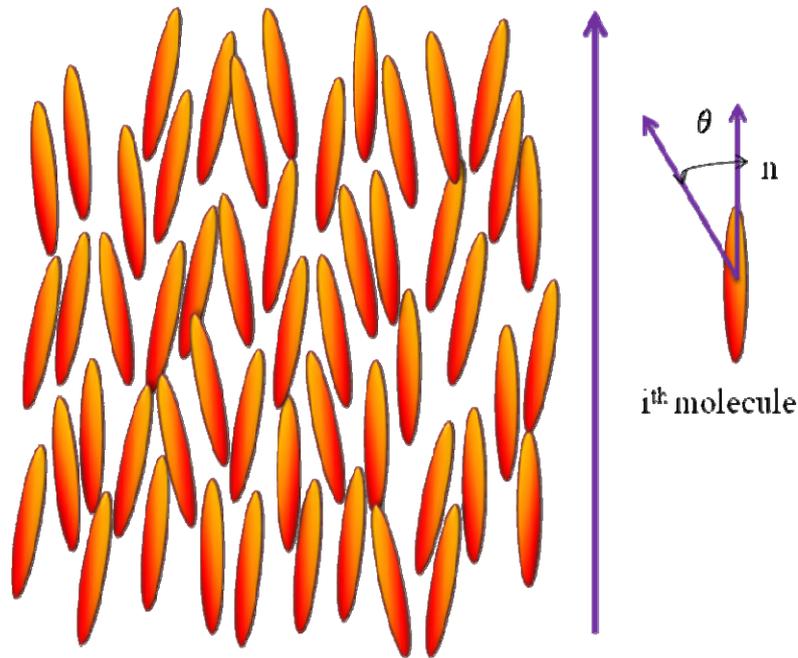


Figure 1.1 Schematic representation of the molecular arrangements in the nematic phase.

On optical inspection under the polarizing microscope for a nematic, some threadlike textures appear from which nematics take their name (Greek “νημα” means thread). In case of uniaxial nematics the magnitude of orientational order along the director \mathbf{n} is defined by a scalar order parameter S [37], which is the average of second order Legendre polynomial with the following form

$$S = \langle P_2(\cos\theta) \rangle = \frac{1}{2} \langle 3\cos^2\theta - 1 \rangle \quad (1.1)$$

where θ is the angle between a molecular long axis and nematic director \mathbf{n} , and the bracket indicates an ensemble average over all the molecules. In the isotropic phase, the distribution of the molecules are random, as a result $\langle \cos^2\theta \rangle = 1/3$ and the order parameter $S = 0$. While in case of perfectly ordered nematic phase the director \mathbf{n} is parallel to the long molecular axis, *i.e.* $\theta = 0$, then $\langle \cos^2\theta \rangle = 1$ and $S = 1$. Theoretically, S varies from $-1/2$ to $+1$, where $-1/2$ corresponds to an unstable state with the molecules perpendicular to the nematic director \mathbf{n} . Practically, S varies from 0.3 to 0.8 and the order is increased with decrease in temperature. In order to obtain the information about molecular ordering in nematic phase the scalar order parameter (S) is not adequate, rather a macroscopic order parameter

(Q_{ij}) which is a real, symmetric and traceless second rank tensor is more useful [7]. For the uniaxial nematic Q_{ij} is given by the following expression

$$Q_{ij} = \frac{1}{2}S(3n_i n_j - \delta_{ij}) \quad (1.2)$$

where, $i, j = x, y, z$ are the axes of the coordinate system and δ_{ij} is the identity tensor. S is defined by the Equation (1.1). The macroscopic order parameter Q_{ij} can be written in a matrix form as follows

$$Q_{ij} = \begin{bmatrix} -\frac{1}{2}S & 0 & 0 \\ 0 & -\frac{1}{2}S & 0 \\ 0 & 0 & S \end{bmatrix} \quad (1.3)$$

1.2.2.2 Cholesteric or Chiral nematic (N^*) phase

In cholesteric liquid crystals the molecules align along the director which rotates in space as the molecules are spontaneously forming macroscopic helical structure (as shown in Figure 1.2). Presence of chiral molecules causes the director profile to trace a twisted configuration through the medium. The distance for which the director rotates through a 360° angle is defined as the pitch [38,39].

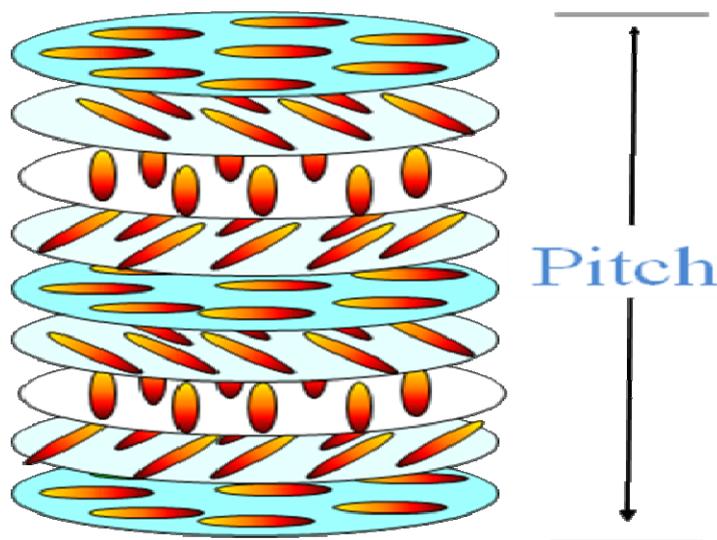


Figure 1.2 Schematic representation of molecular arrangements in the Cholesteric (N^*) phase.

Actually, there is no layered structure and the local ordering is identical to that of the nematic phase. When the length of the pitch is of same order of magnitude of the wavelength of light, visible reflection occurs [40,41]. External influence of stimuli such as temperature, light irradiation, electric fields *etc.* significantly affect the helical pitch. Under polarising microscopy the characteristic fingerprint texture is observed for this phase. Their magnificent colours and optical textures under an applied field make them attractive for flat panel display [42].

1.2.2.3 Smectic phase

The name ‘smectic’ originates from the Greek word ‘σμηγμα’ which means soap, due to the similarities in properties between them. Smectic liquid crystal is one of the distinguished thermotropic liquid crystals and generally occurs at temperatures below the nematics. In this phase the molecules are arranged in layers along with some correlations in their positions in addition to the orientational ordering [43,44]. The molecules in most of the smectics are mobile in two directions and can rotate about one axis. Various molecular configurations and orientations within and between the layers lead to polymorphism of smectic phases *i.e.* smectic A, smectic C, smectic B, smectic E, smectic G, smectic H, smectic F, smectic K and smectic J *etc.* The smectic layers are capable of glide over one another, as a result it shows fluid properties but are much viscous than the nematic phase.

1.2.2.3.1 Smectic A phase

The smectic A (SmA) phase is the least ordered phase among all the smectic phases and possess D_{∞} symmetry [45-47]. The molecules are parallel to each other *i.e.* the director is normal to the plane of the layer and hence exhibit orientational order similar to that of a nematic within a layer (shown in Figure 1.3). Moreover, the centre of mass of molecules are arranged in equidistant planes exhibiting one degree of translational order. The periodic structure is equivalent to a sinusoidal density wave which is given by

$$\rho = \rho_0 \left\{ 1 + \text{Re} \left(|\psi| e^{i(q_0 z + \phi)} \right) \right\} \quad (1.4)$$

where z is along the layer normal, ρ_0 is the average density, $|\psi|$ is the amplitude of the density wave, $q_0 (= 2\pi/d)$ the wave vector, ϕ is an arbitrary phase and d is the layer thickness. The most generally observed natural SmA appearance is the fan-shaped texture or bâtonnets textures [48]. This phase is also recognized by the focal conic texture. Smectic A phase is further classified in smectic A_1 , smectic A_2 and smectic A_d phase [49-51].

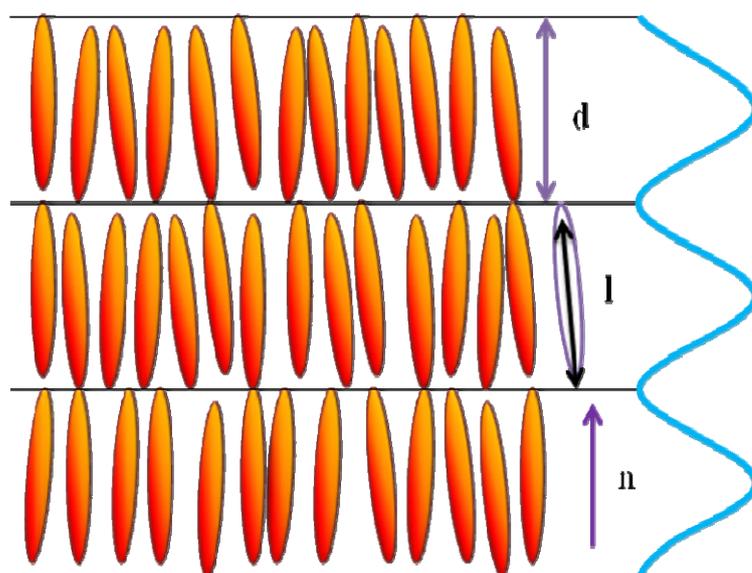


Figure 1.3 Schematic representation of molecular arrangements in the smectic A phase.

In smectic A_1 , also known as monolayer smectic, molecules point up and down randomly within each layer and the layer thickness is equal to the molecular length. In bilayer smectic A_2 phase molecules stack up in layers without overlapping and the molecular dipoles are concentrated in the boundary of alternate layers. The structure repeats itself over a distance equal to twice of the molecular length. Due to the existence of molecular dipole moments they interact with each other and in some cases align themselves by overlapping with each other and form smectic A_d phase. In this phase the layer thickness is in between the mono and bi-layer smectic A phase.

1.2.2.3.2 Smectic C phase

In the smectic C (SmC) phase molecular arrangement are similar to the smectic A phase however the director constantly tilt with an angle to the smectic

plane as shown in the Figure 1.4. This phase is observed at lower temperature than the smectic A phase. Tilting of the director makes an effective shrinkage in the layer spacing of the molecules. The temperature dependent tilt angle breaks the $z = -z$ symmetry seen in the SmA phase and leads to optical, electrical and magnetic bi-axiality. Under microscopic textural observations SmC bâtonnets nucleate, which grow anisotropically and merge to form a texture similar to the fan-shaped appearance of the SmA phase [47]. Often striated texture is observed for direct nematic to SmC phase transition [48,52].

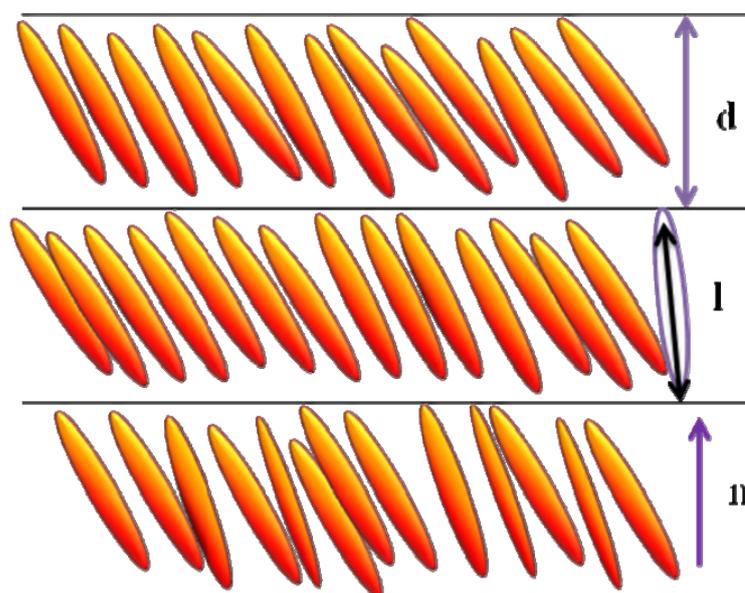


Figure 1.4 Schematic representation of molecular arrangements in the smectic C phase.

1.2.2.3.3 Hexatic smectic phases (SmB, SmI, SmF)

The hexatic smectic phases possess bond-orientational order *i.e.* the centre of mass of molecules within a smectic layer are arranged in an oriented hexagonal grid with long range orientational order of the hexagons, short range positional order within layers and no interlayer positional correlation [53]. There are three distinguished hexatic smectic phases namely smectic B (SmB), smectic I (SmI) and smectic F (SmF) as depicted in Figure 1.5. The smectic B mesophase is arranged with the director perpendicular to the smectic plane, but the molecules are organized into a hexagonal network within the layer. The SmB phase is orthogonal phase while SmI and SmF are tilted phase. The principal difference

between the SmI and SmF phase is that the tilt in SmI is along the hexagonal grid lines, towards the nearest neighbour, while the molecules in SmF tilt towards the next-nearest neighbour 'into' the triangle building up the hexagon [43,44,48,49,54].

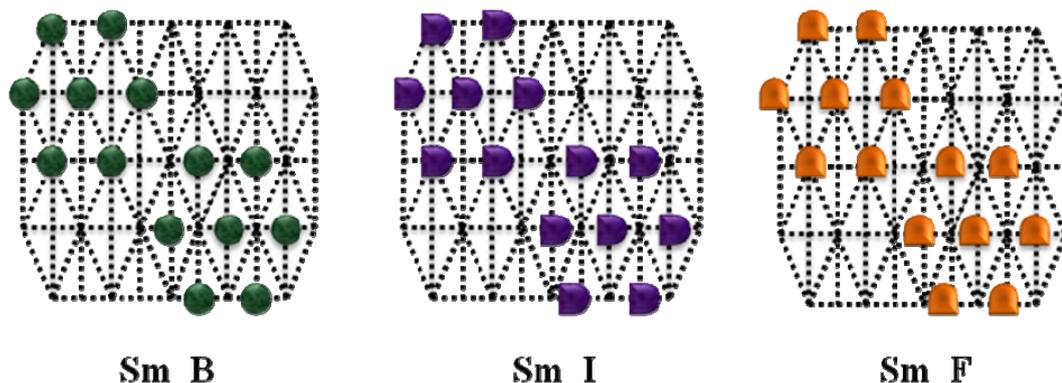


Figure 1.5 Schematic representation of molecular arrangements in the smectic B, smectic I and smectic F phase.

1.2.2.3.4 Soft crystal phases (B, J, G, E, K, H)

In all the soft crystal phases the molecules exhibit long range positional order in addition to the hexatic in-layer translational order. This long range positional order distinguishes the hexatic smectics from the 'smectic-like' soft crystal phases. The most general soft crystal phases are Crystal B, E, G, H, J, K and abbreviated only with the capital letter, without the prefix "Sm". The soft crystal phases possess three dimensional long-range order. In Crystal J and G the rotation of molecules around the molecular long axis is strongly hindered and in the Crystal E, K and H phases the rotational hindrance around the long axes is so strong that only jumps between two favoured positions are allowed [43,48,49].

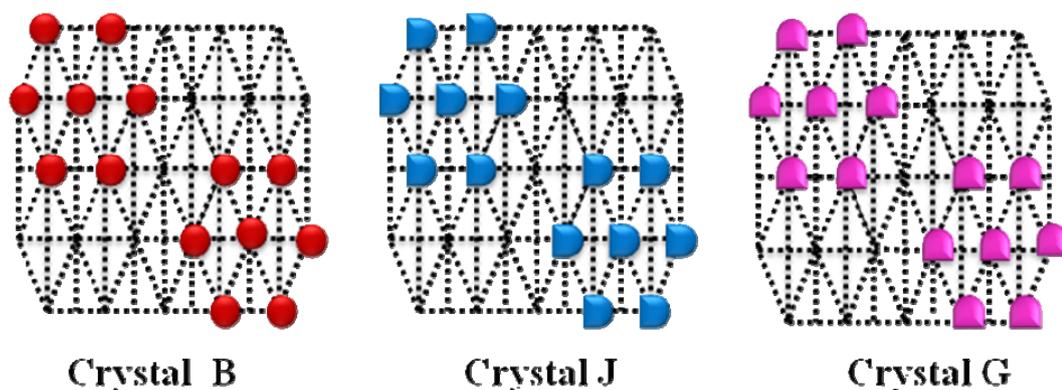


Figure 1.6 Schematic representation of molecular arrangements in the crystal B, crystal J and crystal G phase.

1.2.2.3.5 Chiral tilted smectic phases

The mesomorphic properties and molecular arrangement of the liquid crystalline compounds containing chiral molecules is distinctly different from its achiral version and denoted by a star after the letter, *i.e.* SmA*, SmC* *etc.* [55-57]. These chiral phases possess lack of mirror symmetry. The molecular arrangement of SmA* phase which is composed of chiral molecules is similar to the achiral SmA phase. The SmC* phase is a chiral tilted phase, which tend to form a macroscopic helical structure along with the inclined layers with respect to the layer normal [58-62]. The helix axis must be pointed along the layer normal as a helix within the layer plane is not compatible with a layered structure. The periodicity of the helix, referred as the pitch depends on temperature. Due to helicity, this phase rotate the plane of polarization of linearly polarized incident light along the helix axis and exhibits an unusual strong optical activity. It also selectively reflects circularly polarized light with a wavelength equal to the pitch of the helix. If the pitch length corresponds to visible wavelengths, the sample becomes brightly colored. Moreover, the SmC* phase is spontaneously polarized, with the polarization parallel to the layers but perpendicular to the tilt plane [58].

In the SmC_A* phase, the molecules in the neighbouring layers almost tilt in opposite direction [63-65]. Thus, the spontaneous polarization in the neighbouring layers pointed in the opposite sense of the direction and perpendicular to the tilted plane. The tristate switching characteristic of SmC_A* phase is potentially applied to achieve easy gray scale switching in display devices [60,66]. Moreover, wide viewing angle with a relatively large contrast ratio, inherent DC compensation and fast response time make antiferroelectric liquid crystals superior to ferroelectric liquid crystals. Nowadays high tilted or orthoconic antiferroelectric liquid crystals are used to remove its initial linear response and high quality alignment problems [67,68].

Except SmC* and SmC_A* phase, three different thermodynamically stable sub-phases SmC_α*, SmC_β* SmC_γ* which belong to the chiral smectic C family have been reported [69-72]. The phase sequence generally observed on cooling is



Several theoretical models *viz.* one-dimensional Ising model, two-dimensional XY-model (clock model) by Cepic and Zeks [72] have been proposed for the variety of SmC^* structures. The molecular arrangements in the SmC^* and SmC_A^* phase are illustrated in Figure 1.7.

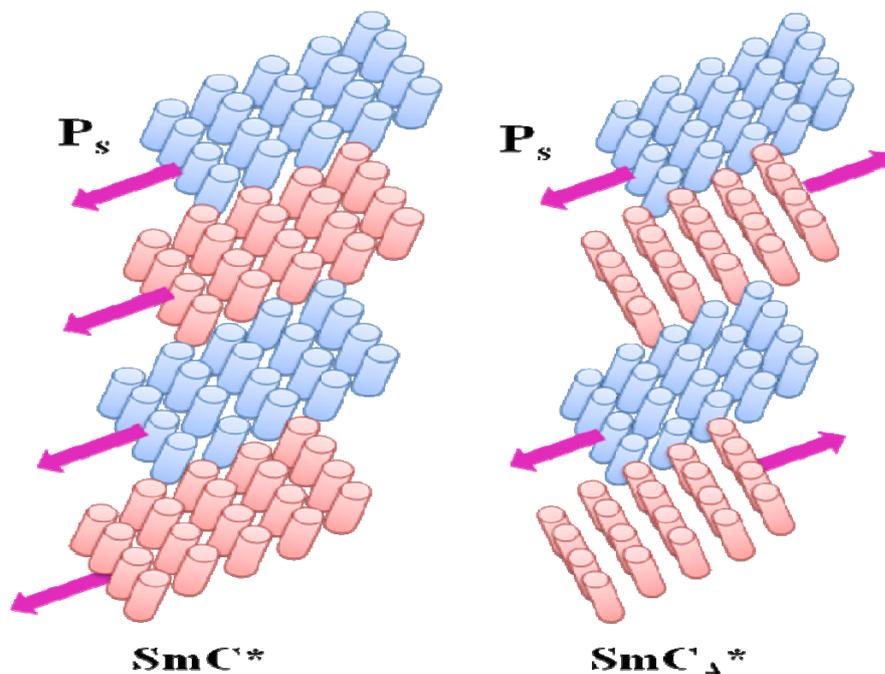


Figure 1.7 Schematic representation of molecular arrangements in the ferroelectric (SmC^*) and antiferroelectric (SmC_A^*) phase.

1.2.3 Other liquid crystalline phases

1.2.3.1 Discotic phase

Among different types of liquid crystals, discotic liquid crystals [73-75] are a promising class of materials, consisting of diskshaped molecules with rigid aromatic core which is surrounded by flexible aliphatic chains. The aromatic core provides structural stability by intermolecular interaction forces *i.e.* van der Waals, dipolar and charge–transfer interactions force. Actually, these molecules interact through π -orbital interactions and self-organize into a regular 2-dimensional lattice. Discotic liquid crystals may exhibit a nematic phase, with orientational ordering but does not possess positional ordering between the constituent molecules. Unlike the calamitic nematic phase, the short molecular axes orient more or less parallel to each other and their centre of mass are isotropically distributed in the discotic nematic phase. In columnar discotic phase molecules

stack, core on core, to form a hexagonal array of molecular columns with some degree of positional order as depicted in Figure 1.8. The electrical conductivity in this phase is highly anisotropic, with the axial conductivity being up to 100 times greater than the in-plane conductivity. Addition of chiral dopant or chiral discotic molecules leads to a further helical ordering of molecules in each column and form chiral discotic nematic phase. Recently, discotic liquid crystals are widely used in light emitting diodes, photovoltaic cells, photoconductors and field effect transistors due to their excellent processability, high charge transport, self-healing and self-organization power [76,77].

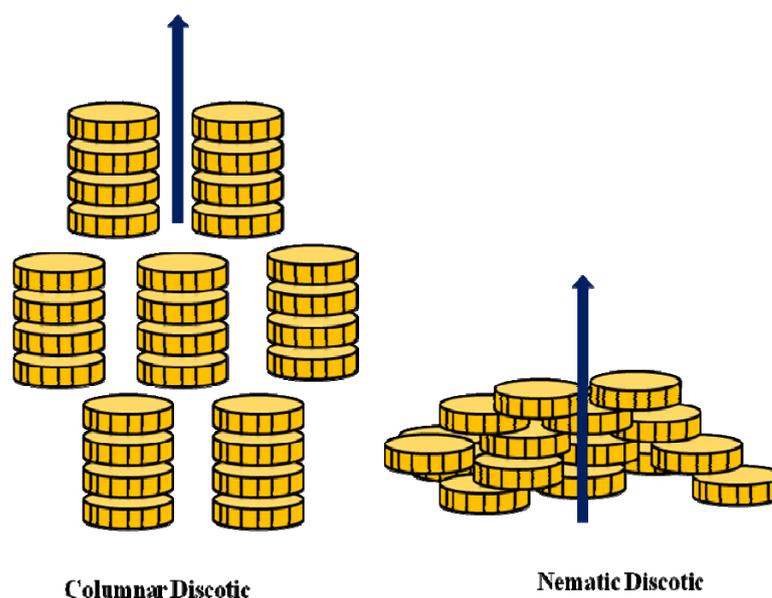


Figure 1.8 Schematic representation of molecular arrangements in the discotic phase.

1.2.3.2 Blue phase

Blue phase (BP), located in between the isotropic liquid and chiral nematic phase have been growing interest as a unique class of frustrated liquid crystalline material [78,79]. The structure of the blue phase can be explained in terms of the defect in a cubic array. In blue phase two double twist cylinders, arranged in two mutually perpendicular directions placed to form a continuous director field and a third double twist cylinder is merged through the creation of a defect. These defects built a cubic lattice with lattice parameters of several hundred nanometres. Blue phase are classified in three distinguished category: BPI exhibits a cubic body centred structure; BPII has a simple cubic unit cell and BPIII has structure

close to the isotropic liquid. A schematic structural image of BPI and BPII is depicted in Figure 1.9. Blue phases do not exhibit double refraction but show optical activity and selective reflection of circularly polarised light. This is thermodynamically stable frustrated phases; exists over a narrow temperature range. However, recent progress in stabilising blue phase over a wide temperature range using polymer dispersed liquid crystal have been developed [79]. From application point of view it possesses some revolutionary features *i.e.* sub-millisecond response time, an isotropic dark state and no need of surface alignment. Utilizing the electric field induced birefringence now a days blue phase is widely employed in next generation liquid crystal display technology [80,81].

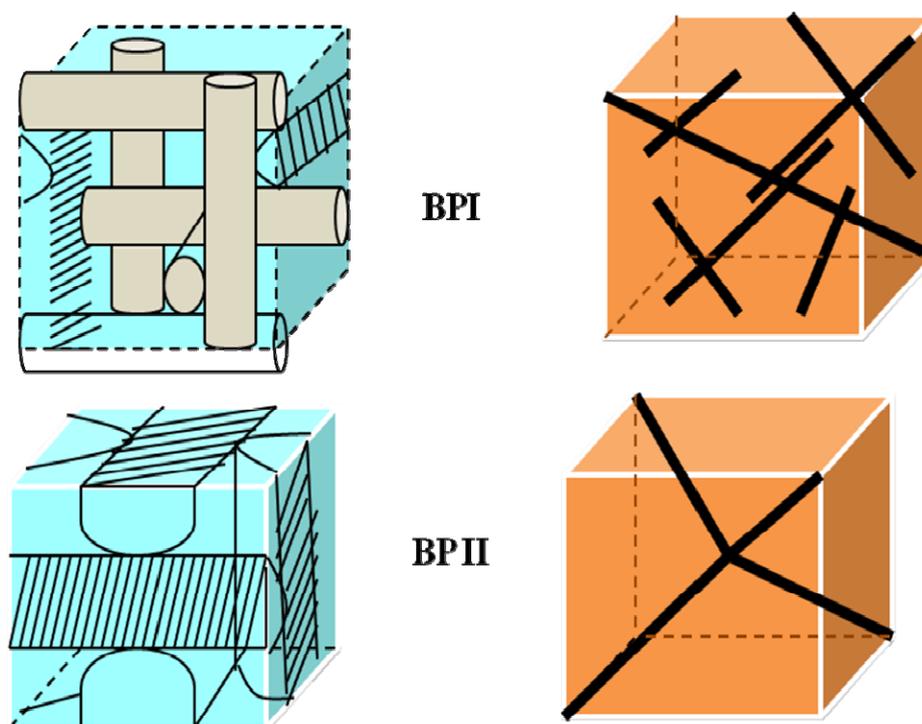


Figure 1.9 Schematic representation of blue phase structure showing blue phase I (BPI) and blue phase II (BPII).

1.2.3.3 Twist grain boundary (TGB) phase

Twist Grain Boundary (TGB) phases occurs in between cholesteric and fluid smectic phases [82,83]. Chiral compounds tend to form a helical structure whereas molecular interactions favour a layered structure. Incompatibility of helical superstructure with the smectic layering are responsible for this frustrated phase having regular arrays of screw dislocations mediated blocks of smectic

order (smectic A or smectic C) [84,85]. This phase is analogous to the Abrikosov flux lattice phase of a type II superconductor [82,86]. A schematic representation of the TGB structure is depicted in Figure 1.10. The length of pitch is in the order of a few micrometers.

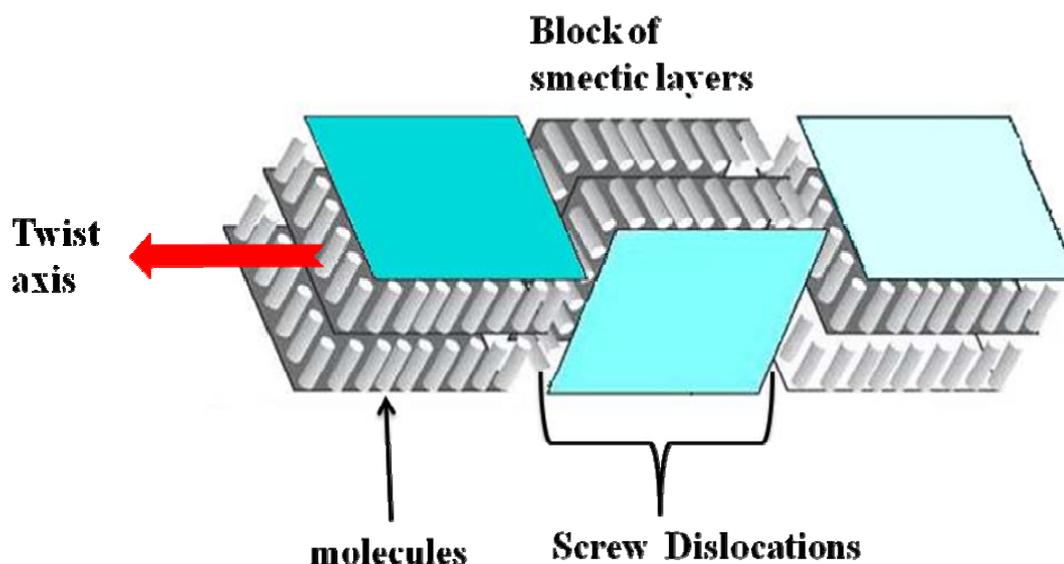


Figure 1.10 Schematic representation of molecular arrangements in the twist grain boundary phase.

1.2.3.4 Polymer stabilised liquid crystals

Polymer stabilised liquid crystal is an interesting and innovative topic in liquid crystal research. It transfers the self-organised liquid crystalline order onto a polymer network by photo-polymerisation of bi-functional mesogens in the liquid crystal host phase. Also they intrinsically respond to external stimuli such as temperature variation and magnetic fields. Some outstanding developments in the field of polymer stabilised liquid crystals have been developed not only for academic interest, but also of interest for future display and photonics applications [87-89].

1.2.3.5 Bent core liquid crystals

In 1996, bent-core or banana shaped liquid crystal was first reported by Niori *et al.* [90]. The constituent molecules of these mesophases are achiral however these molecules form chiral superstructures in their LC mesophases and

show polar order. The lateral correlation of the molecular dipoles yields this polar order within the layers, which can be switched on by applying an electric field [91-93]. Generally, such phases are composed of molecules with rigid bent aromatic core or mesogenic dimers with an odd-numbered non-cyclic (flexible) spacer unit or hockey-stick shaped molecules, where an alkyl chain is attached to the meta-position at one end of an aromatic core as illustrated in Figure 1.11. Seven mesophases were explored and denoted by B1–B7, where “B” indicates for bent, banana, bow or boomerang. This new way to macroscopic polar order and chirality immediately draw a great interest of liquid crystal research [94,95].

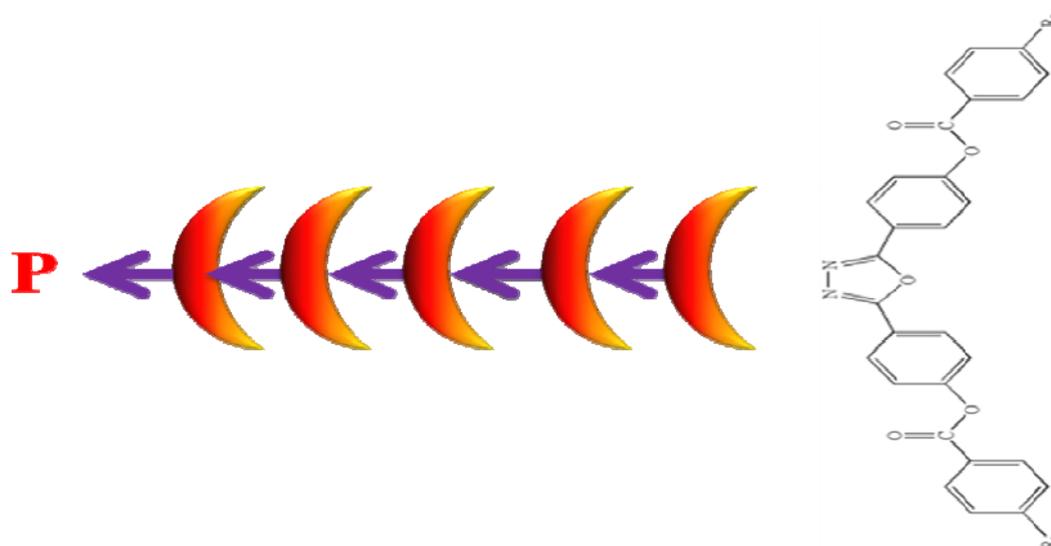


Figure 1.11 Schematic representation of bent core liquid crystals.

1.2.3.6 Supramolecular liquid crystals

Supramolecular liquid crystals are a unique self-assembled structure which is a combination of discrete low molecular weight materials with those of polymers in their ability to form secondary and tertiary structures [96,97]. Due to their variety of physical properties they are potentially attractive for applications in the fields of nanoscience, materials and biology. With the aid of hydrogen bonding or ionic interactions well-defined structures such as rods and disk shaped molecules made dimer, trimer, spheroid *etc.* through self-assembly of two or more complementary molecular components. They are responsive to external stimuli as well as different environments and modify their self-assembled structures by the dissociation and association of non-covalent interactions. Thus, super- and supra-

molecular liquid crystals provide unique materials for the study of the structures and properties of self-organizing and self-assembling processes [98,99].

1.2.3.7 Twist-bend nematic liquid crystals

The nanostructured twist-bend nematic (N_{tb}) phase is a new condensed phase of matter with unique properties [100,101]. This new heliconical phase has been reported in various bent shaped LC dimeric compounds containing flexible methylene spacers and rigid bent-core molecular materials. Interestingly, they form chiral structures with a very short pitch in the order of 10nm even from the achiral molecules, such as tilted polar smectic phases of bent-core molecules. The twist-bend nematic phase under an applied electric field exhibit very fast polar switching. From X-ray diffraction it is found that the N_{tb} phase lacks the mass density modulation characteristic of a true smectic and referred as pseudo-layered structure. This intriguing phase occurs below the conventional nematic phase over a wide temperature range extending to ambient temperatures.

1.3 Nano dispersed liquid crystals

Currently liquid crystal research has made huge contributions to nano science and nanotechnology and a new field *i.e.* liquid crystal nano science has gained growing interest. LC compounds are very sensitive to external perturbations and their physical properties can be suitably tuned by preparing binary mixtures or embedding nanoparticles into the liquid crystalline matrix [102-106]. Nano-particles of different sizes, shapes and compositions that are smaller than the liquid crystal molecules may significantly affect the phase behavior by their interactions with the liquid crystal molecules. The liquid crystalline compounds are commonly doped with metallic platinum nanoparticles, carbon nanorods, aerosil particles, CdSe/ZnS core-shell, quantum dots and CdSe quantum dots *etc.* The doped nano particles preferentially lie in regions where the long axes of the liquid crystal molecules are aligned parallel to the substrate. Development of such hybrid systems having mixtures of liquid crystalline compounds with nano particles at different concentrations [107-111] proved to be a useful technique to enhance the optical as well as some other physical properties of the host LC

materials. Moreover, study of the different thermal parameters of nano doped liquid crystals has attracted a new interest owing to their consequence for several application devices based on the electro-optical properties of the same.

1.4 Liquid crystalline mixtures

Numerous liquid crystalline compounds have been synthesized so far but it is very difficult to fulfil all the desired physical properties with a single liquid crystal sample. Hence, mixtures of liquid crystalline compounds are often prepared [112-116] where the concentrations of the pure compounds are suitably tuned so that better materials may be produced for applications. In particular, mixing of two LCs that are different from each other can strongly affect the physical properties such as birefringence, dielectric permittivity, dielectric anisotropy, elastic constant, threshold voltage *etc.* and also the phase behavior of the mixtures compared to the pure compounds. Moreover, understanding the molecular interactions between different compounds can be of fundamental importance to be able to tune the physical properties of liquid crystals.

On the other hand, the binary mixtures of LCs are also used to study the various phase transitions and critical phenomena in the field of liquid crystal research [117-121]. Preparation of such binary mixtures by selecting suitable compounds with certain mesomorphic range offers a unique way to construct a phase diagram which is of fundamental interest for understanding the phenomena of phase transitions in soft matter. By changing the concentration of the guest or host materials the range of different mesophases can be controlled.

1.4.1 Induced phases

Physical properties of individual mesogens undergo some deviations in their mixtures. These deviations become characteristic thus making the study of mixtures very significant. Sometimes the thermal stability of a liquid crystalline phase may be enhanced and a new phase of higher order may be created. This formation of new mesophase in binary LC mixtures is known as the induction of phase and the newly created phase is known as the induced phase [50,122]. The reverse phenomena may also occur where the thermal stability decreases and a new phase of lower order may be formed [50].

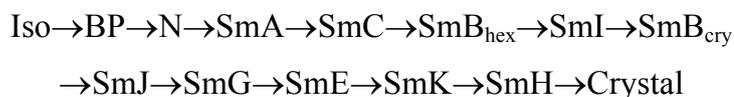
Smectic phases existing in pure compounds decrease their smectic stability while forming the binary mixtures and lower order nematic phases are created. These phases are known as the induced nematic phases [123]. Induced nematic phases are generally formed in binary mixtures of smectogenic compounds. Mixtures of two polar smectogenic LCs, where one of them possesses monolayer smectic A (SmA_1) phase and the other partially bilayer smectic A (SmA_d) phase, shows a depression of smectic phase stability with the emergence of a nematic gap between them [124-126]. On the other hand, strong induction of smectic phase has been observed in mixtures of two nematogens having terminal polar group [127,128]. Smectic phase can also be induced in mixtures of polar-non polar [127,129-131] nematogens as well as in mixtures of non polar LC compounds [122,132,133].

The induction of a phase in liquid crystalline mixtures depends upon several intermolecular factors such as van der Waals forces, steric forces, electron donor interactions, hydrogen bonds and also on the charge-transfer interaction between the components of the binary mixtures. Therefore, it is hard to develop a general theory that could be able to describe the behavior of the mixtures. Several attempts have been made to describe the induced phase behavior [127,128,134-142]. In induced nematic systems orientation of the dipoles of the terminal polar groups plays a major role for suppressing the smectic phase stability [50]. Again a growing difference between the smectic layer spacings of the pure compounds is accountable for depressing the smectic phase stability owing to the increase in frustration of the smectic lattice after mixing [50,124,126,143]. For the higher order induced smectic phase de Jeu *et al.* [138] suggested a molecular model based on the mean field approximation for the cyano compounds. The dispersion interactions and charge transfer complex formation in which the cyano compounds acts as electron acceptor are responsible for the appearance of induced smectic phase. Moreover, Chiu *et al.* [141] have divulged that the strong nematic interaction between the different liquid crystalline compounds can lead to a more stable nematic phase in the nematic mixtures compared to that in the pure compounds with the same mesogenic moiety. To explain an induced smectic phase boundary in the mixtures of pure nematogens, Kyu *et al.* [142] have build up a theoretical model by combining the Flory-Huggins theory for isotropic mixing

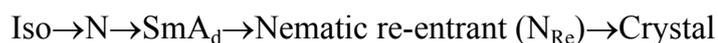
[144] and the Maier-Saupe-McMillan theory for ordering of the smectic A phase [21-24] in nematic mixtures. According to this model, a strong mesogenic interaction could induce a smectic phase even though the smectic ordering was not present in the pure compounds. Sharma *et al.* [127], Schneider *et al.* [139], Araya *et al.* [128,145] and Iida [137] also explained the induction of smectic phases on the basis of charge transfer bands in mixtures and attributed an immense significance to the donor-acceptor interactions.

1.4.2 Re-entrant nematic phase

The mesogenic compounds show a rich variety of polymorphism. By transforming the symmetry of the system they can transit from one mesophase to another mesophase of different order. Increase in the temperature causes progressive destruction of the molecular order and the high symmetric liquid crystalline phase occurs at high temperature region. If a mesogen exhibits all the liquid crystalline phases then on cooling the following phase sequence is expected



In practice a small part of the above phase sequence occurs in most of the LC materials. In some cases less ordered mesophase re-appears in between two higher ordered mesophases. This phenomenon is well known as re-entrant polymorphism. In 1975 Cladis [146] discovered re-entrant nematic phase in binary mixtures of two strongly polar compounds namely cyanobenzilidene octylxylaniline (CBOOA) and hexyloxybenzilidene aminobenzonitryle (HBAB). The phase sequence of transition on cooling is as follows



Numerous compounds with different re-entrant phase sequence *i.e.* N-SmA_d-N_{Re}, N-SmA_d-N_{Re}-A₁ or multiple re-entrance behaviour (N-SmA_d-N_{Re}-SmA_d-N_{Re}-A₁) is reported by many researchers [147-152]. The re-entrancy is not only found in strong polar system but also in systems consisting of low polar calamatic [131] or discotic [153] compounds and also in mixtures of high and low polarity

compounds [154,155]. A considerable volume of experimental and theoretical work has been devoted to explain the re-entrant phase behavior [156-159].

1.5 Phase transition

Transformation between the various phases of matter are one of the most spectacular and remarkable macroscopic events in nature. Phase transition is the transformation of a thermodynamic system from one phase to another as a function of some externally imposed constraints such as temperature, pressure, concentration, magnetic field *etc.* At phase transition a system goes through a qualitative change developing some molecular ordering which was not present before. When a system changes its state from one phase to another, there will be a point where the free energy does not varies smoothly *i.e.* it is a non-analytic function at that point. Owing to this non-analytic nature, the free energy on either side of the transition point are two distinct functions, accordingly the thermodynamic properties will behave in a different way after the phase transition. The common examples of the phase transitions are melting of solid to liquid, freezing of liquid to solid, boiling of liquid to gas and condensation of gas to liquid. If the driving parameter is temperature, the high-temperature phase is always more disordered, *i.e.*, has a higher symmetry than the low-temperature phase [160,161].

Phase transition often involves the development of some type of ordering with an associated symmetry breaking. This broken symmetry can be described by an order parameter which generally increases on decreasing the temperature and measures the degree of molecular ordering as the phase transition progresses. The order parameter is a physical observable parameter which is correlated to first derivative of the Gibbs free energy (G). The actual form of the order parameter is different for different systems. It is defined in such a way that it becomes zero in the disordered phase and possesses non-zero values in the ordered phase. For perfectly ordered state it is assumed to be equal to unity. Examples of the suitable order parameters are the magnetization for a ferro-magnet, electrical polarization for a ferro-electric, pair wave function for a superconductor, density difference for fluid, ground state wave function for the super fluid He⁴ while the degree of

molecular ordering [4] is the most convenient order parameter for the nematic liquid crystals.

Paul Ehrenfest [162,163] classified the phase transitions on the basis of degree of non-analyticity involved in the Gibbs free energy (G). Keeping the other intensive variables constant if the n^{th} order derivative of G with respect to the temperature (T) is discontinuous, then the transition is said to be n^{th} order. The discontinuity in $(\partial G/\partial T)_P$ involves the change in the entropy between the two phases. Therefore, in case of first order phase transition (*i.e.* $n=1$) entropy is discontinuous while for the second order phase transition (*i.e.* $n=2$) entropy is continuous at the transition, but its first derivative is discontinuous across the transition temperature. Under the Ehrenfest classification one can obtain phase transitions above the second order *i.e.* third, fourth and also higher order phase transitions. However, according to the modern classification [164] there are two types of phase transitions *i.e.* first order and second order or continuous phase transition. The first order phase transitions are those which involve latent heat and discontinuity in the thermo-dynamical parameters. While the second order or continuous phase transition is not accompanied by latent heat at the transition. Sometimes the change in the order parameters is also considered in identifying the order of the phase transition [8]. The phase transitions can either be first order or second order depending on the change in the order parameters *i.e.* discontinuous or continuous respectively in the vicinity of transition.

Moreover, liquid crystals are the experimental systems with exceedingly rich phase behavior. The intermediate molecular ordering of LCs makes them very much interesting from the practical as well as theoretical point of view. Several characteristics of phase transition and critical phenomena such as second order or first order transitions, order parameters of diverse symmetries, coupled order parameters, tricritical point (TCP), multi-critical points, wide critical domains, multiple re-entrance behavior *etc.* are frequently observed in liquid crystalline systems, for which this unique state of soft condensed matter is considered as a ecstasy of the physics of phase transitions. The transitions in LCs are generally second order or weakly first order in nature. Hence, they are accompanied by critical phenomena [4,121] exhibiting an unusual behavior near the transition or critical points, for instance increase in susceptibility, fluctuation of order

parameter, an anomaly in the specific heat *etc.* In the field of liquid crystals the critical phenomena has some specific characteristics because of the diversity of the symmetries associated with different phases and the coupling of various order parameters. Furthermore, there is a crossover from one type of critical behavior to other.

1.6 Symmetry

The change of some thermodynamic parameters (for example temperature) of a system can induce a change in the order or disorderness of the system under study. At the high temperature phase a system is in its most disordered state *i.e.* a phase with high symmetry. But as the temperature is decreased, at a particular point the symmetry breaks spontaneously and the system transforms from one phase to another phase. The new phase is more ordered than the previous one but with a lower symmetry. Therefore, most of the phase transitions take place between the phases with different symmetry configurations [165]. On cooling, the LCs successively break the continuous symmetry of the isotropic liquid phase and encompass symmetries that lie in between the highly symmetric liquid phase and low symmetric crystal phase. In the nematic phase the constituent molecules tends to align along a particular direction *i.e.* the director, breaking the continuous orientational symmetry of the isotropic liquid phase while in the smectic A phase the translational symmetry breaks along one direction in addition to the orientational symmetry.

1.7 Critical exponents and universality class

The critical behavior near phase transition refers to the singular character of various physical properties of a system under some particular conditions. These conditions may be temperature, pressure, electric field or magnetic field. However, the classical critical phenomena is generally concerned with the magnetic or liquid-gas systems, but critical behavior near the transitions in some other thermodynamic systems for example superconductors, super fluids and also liquid crystals, has attracted an immense interest and enhanced this particular field of physics. The main difficulty in the theory of phase transition is to study the behavior of a system in the vicinity of transition or critical point. Near the

transitions most of the physical quantities pertaining to the system demonstrate a power law behavior that can be characterized by a set of parameters known as the critical exponents [166-168]. These exponents illustrate the non-analyticity of various thermodynamic functions and determine the qualitative nature of the critical behavior of a system. The defining relations of various critical exponents are given in the Table 1.1. Moreover, the critical exponents are not completely independent rather they are related by some scaling relations or inequalities which follow from the fundamental thermodynamic considerations.

Table 1.1 Some standard critical exponents and their defining relations

Measurable physical quantity	Critical exponent	Defining relation
Heat capacity ($t < 0, t > 0$)	α	$C(T) \sim t ^{-\alpha}$
Susceptibility ($t < 0, t > 0$)	γ	$\chi(T) \sim t ^{-\gamma}$
Correlation length ($t < 0, t > 0$)	ν	$\xi(T) \sim t ^{-\nu}$
Order parameter ($t > 0$)	β	$S(T) \sim t ^{-\beta}$

[#] t is the reduced temperature = $(1-T/T_C)$, T_C is the transition temperature

The critical exponents are universal in nature and it depends only on the dimension of the system, the range of interaction (whether long range or short range) and the number of components of the order parameter [165]. They do not depend on the fundamental microscopic features or the details of the molecular interactions of the system. A consequence of this is that completely dissimilar systems can demonstrate the identical critical behaviour. Therefore, phase transition of very different systems with different microscopic configurations often described by a same set of critical exponents. This occurrence is commonly known as universality and the systems that exhibit the same set of critical exponents are said to belong to the same universality class [164,166]. The concept of universality class is an insight of the renormalization group theory of phase transition. Moreover, these ideas of universality are also applicable to the several phase transitions in liquid crystals.

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